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SAH02411GB

2. Patent application number

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3. Full name, address and postcode of the or of each applicant (underline all surnames)

5956809004

Cambridge University Technical Services Ltd
The Old Schools
Trinity Lane
Cambridge
CB2 1TS

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

Terahertz Spectroscopy

5. Name of your agent (if you have one)

Gill Jennings & Every

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Broadgate House
7 Eldon Street
London
EC2M 7LH

Patents ADP number (if you know it)

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Number of earlier application

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Description 7

Claim(s)

Abstract

Drawing(s)

5 *TS* *JK*

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Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

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NO

11. For the applicant

Gill Jennings & Every

I/We request the grant of a patent on the basis of this application.

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6 September 2002

12. Name and daytime telephone number of person to contact in the United Kingdom

HALEY, Stephen

020 7377 1377

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TERAHERTZ SPECTROSCOPY

Over the past few years, there has been much interest in developing the technique of difference spectroscopy for the investigation of photo-biological systems. 5 Examples of such systems include bacteriorhodopsin and rhodopsin, as well as the study of photosynthetic reaction centers in bacteria and plants. The principle behind difference spectroscopy consists of recording infrared spectra (of, for example, a protein) in two different states, before and after applying an external perturbation such as light. The difference is then calculated, and only vibrational modes that change in 10 intensity or frequency are identified in the difference spectrum. Signals that do not originate from groups affected by the perturbation are subtracted out. This technique is particularly effective in probing minute structural differences between two states.

Light-induced difference spectroscopy (based on Fourier transform infrared (FTIR) technology) has been developed and applied successfully to investigate the 15 structural changes associated with individual bonds of chromophores and proteins. The detection sensitivity (defined as $\Delta T/T$, where T is the transmission coefficient) achieved in the mid-infrared frequency range is 10^{-5} - 10^{-6} , at fixed delay and frequency, although greater sensitivity is required to apply difference spectroscopy to other important photo-biological systems. In the far-infrared, however, the poor 20 performance of FTIR spectrometers, owing to the lack of suitable sources and detectors, makes it impractical to develop a FTIR difference spectroscopy system.

Recent advances in terahertz (THz) time-domain spectroscopy have, though, stimulated interest in developing light-induced THz difference spectroscopy. Key 25 benefits of such spectroscopy include the acquisition of time-resolved data and coherent detection. These give the amplitude and phase of the THz field, rather than simply the laser intensity. The dynamic range of coherent THz detection has been reported to be 10^5 - 10^8 , corresponding to an intensity range of 10^{10} - 10^{12} . Such a high dynamic range together with the intrinsic advantage of time resolved coherent detection make the THz time-domain system attractive for differential spectroscopy.

30 There has also been proposed differential THz time-domain spectroscopy for the characterization of thin dielectric films. In this approach, a mechanical shaker is used to exchange rapidly the sample of interest and a reference sample at a frequency of 20 - 100 Hz. The small difference between the THz pulses transmitted through sample and reference was monitored with a lock-in amplifier. Extremely high

sensitivity, of the order $\Delta T/T \approx 10^{-9}$, is apparently possible but the requirement for a mechanical shaker limits the practicality of the device and makes it difficult to control and potentially unreliable.

5 According to the present invention there is provided a terahertz spectroscopy system comprising:

a terahertz source for exciting, in use, a sample with a pulse of radiation in the terahertz frequency range;

10 excitation means for providing excitation energy in the form of an electromagnetic or acoustic wave during illumination of the sample by the terahertz source;

a terahertz sensor for receiving energy from the illuminated sample; and

15 processing means for receiving signals from the terahertz sensor and processing them to provide an output representative of the terahertz spectrum received by the sensor.

20 The excitation means may be a laser and may be a low power laser. The laser may also provide the terahertz source.

Optical components may be provided in the system in order to focus the terahertz radiation onto the sample and also onto the terahertz sensor.

25 Means may be provided for controlling the direction of the exciting energy to scan it across the surface of the sample in use. Corresponding means may be provided to control the illumination of the terahertz radiation in order to enable scanning of this also across the sample.

There may also be provided means for focussing or localising the exciting energy in order to control its spatial resolution and hence control the overall spatial resolution of the system.

An example of the present invention will now be described with reference to the accompanying drawings, in which:

30 Figures 1a and 1b are graphs showing the output form an example system according to the present invention when measuring a semiconductor surface and an output of an example system according to the invention showing peak amplitude versus time delay;

Figure 2 is a graph showing measured terahertz signal transients for the same semiconductor material as employed in figure 1 for both unexcited (open circles) and excited (lines) samples;

Figure 3 is a diagram showing a molecular structure of a copper dye molecule sample employed in a measurement using an example system of the present invention;

5 Figure 4 shows two graphs indicating outputs of an example system according to the present invention when measuring the sample of figure 3;

Figure 5 is a plan view of a sample being illuminated by the system of the present invention;

10 Figure 6 is a side schematic diagram showing the system of the present invention; and

Figure 7 shows a plan view of a semiconductor sample and an output of the system according to the present invention showing clearly the increased resolution of the system as it passes from a first to second material.

Referring now to the figures, an example system according to the present invention will be described, together with two example experiments using that system.

15 Referring to figure 6, a system 1 according to the present invention has a terahertz source 2 which is focussed through optical optics 3 onto a sample 4. The sample 4 is also illuminated by an exciting energy source 5, which in this case a pumped Ti:sapphire laser. Additional optional optics 6 focus terahertz radiation passing through the sample 4 to a terahertz sensor 7 which provides an output to 20 processing means 8.

25 As can be seen from figure 5, the terahertz radiation generated by the terahertz source 2, which may be the laser, can be scanned across the surface of the sample 4 whilst the laser beam 5 is also scanned within the confines of the spot defining the terahertz radiation, such that the whole surface of the sample can be evaluated in a controlled manner

30 Much of the arrangement of a spectroscopy system according to the invention is similar to that for visible-pump-THz-probe experiments. The laser 6 is provided and produces visible/near-infrared pulses of, in this example, 12 fs duration at a centre wavelength of 790nm. The output is split into three parts: a 250 mW beam is used to excite a sample with a focus diameter of 300 μ m at a variable time delay with respect to the THz pulse; a 250 mW beam is focused onto the surface of a biased Si-GaAs emitter for THz generation; and the remaining 25mW serves as the probe beam for electro-optic detection using a 1-mm-thick ZnTe crystal.

The laser energy used to excite the samples is only a few nJ, rather than the few μ J used in most pump-probe experiments. This feature has additional benefits in that low energy pulses are less likely to damage the samples under investigation, which is of a particular concern for some biomedical samples.

5 This light-induced THz time-domain difference spectrometer system of the invention can be operated in two ways. The first, and simplest, approach is to use the THz spectrum of the sample in its ground state (without laser excitation) as the reference, and compare this with the spectrum of the sample under laser excitation. The latter can be achieved by electrically chopping the THz beam 2 whilst maintaining
10 constant pump laser excitation. The difference THz spectrum is then calculated, and only vibrational modes that change in intensity or frequency are detected in the difference spectrum. Signals not originating from groups affected by the laser excitation are subtracted out.

15 In the second approach, if the photogenerated process under investigation is fast and highly reproducible, the difference THz time-domain spectrum is measured directly, with a much higher sensitivity. In this case, the pump beam 5 exciting the sample is chopped by a mechanical chopper whilst the THz beam 2 is kept constant. The idea is to monitor the small THz transmission difference between the two sample
20 states by alternately measuring the THz transmission through the excited and unexcited sample, and monitoring the difference signal with a lock-in amplifier. Owing to the intrinsic advantage of the coherent THz generation and detection, detection levels of the order $\Delta T/T \approx 10^{-8}$ can be demonstrated, which is already 2 – 3 orders of magnitude better than the performance of known FTIR spectroscopy systems.

25 Two examples of use of the present invention will now be described to aid understanding of its benefits.

Example one, semiconductor sample. In order to evaluate the performance of the light-induced THz time-domain spectrometer of the invention, Si-GaAs and HR-silicon wafers were studied using the second approach discussed above. Fig. 1 (a) shows the measured THz signal without the pump laser pulse and the differential
30 THz signal 5 ps after visible laser excitation for Si-GaAs. The amplitude of the differential THz signal is less than 2 % of the original THz signal because only a 2 nJ pulse was used for excitation, corresponding to an energy density of about 3μ J/cm². The peak amplitude of the differential THz pulse was monitored as a function of time

after the visible laser excitation and is plotted in Fig. 1 (b). A 50 ps lifetime was calculated by fitting the experimental results.

The differential THz signal arrives at the detector about 100 fs later than the original THz signal, as shown in Fig. 1 (a). This can be explained as follows. The 5 generated THz pulse is collected and focussed onto the sample surface by two parabolic mirrors. Owing to diffraction during the THz wave propagation, the lower frequency components of the THz pulse will focus to a larger spot size at the sample surface than the higher frequency components. The visible pump laser has a spot diameter of 300 μ m and only this pumped area of the sample will produce the 10 differential THz signal. The spatial confinement of the differential THz pulse in the pump area thus acts as a spectral filter, shifting the frequency distribution of the transmitted THz pulse towards higher frequency. This reshapes the THz waveform and, owing to the normal dispersion, slows the THz pulse down so that it arrives at a later time. The shape and peak position of the differential THz signal can be well 15 simulated by applying a high-pass digital filter to the original THz signal, confirming that the effect of a spectral filter is to cause the later arrival of the differential THz pulse.

In contrast to our observations here, Schall et al. observed the THz pulse to arrive earlier when transmitted through an optically excited Si-GaAs wafer. This is a 20 result of the different experimental arrangement used. It has been known to measure the THz pulses transmitted through an unexcited and a continuously excited GaAs wafer. In this case, the frequency-dependent transmission and phase shift at the air-GaAs (excited) interface has a substantial contribution to the observed earlier arrival of the THz pulse. Indeed the earlier arrival of the THz pulse for excited 25 HR-silicon wafers is shown in Fig. 2. For a silicon wafer the lifetime of the photo-generated carriers is much longer than the time interval between two successive optical pulses (12 ns). A much larger differential THz signal is observed owing to the accumulation of photo-generated carriers in the silicon. Considering that HR-silicon is widely used in THz time-domain spectroscopy experiments, care must be taken to 30 avoid the frequency-dependence of the transmission and phase shift caused by long-lived photo-generated carriers. Note that the effective spot size of the pump beam on the sample surface in this case is much larger owing to the diffusion of the photo-generated electrons.

In summary, for GaAs wafers, we directly measured the differential THz signal resulting from optical excitation. The differential signal is only a small fraction (1 – 2 %) of the original THz signal, therefore, the contribution from the frequency-dependent transmission and phase shift at the interface is much smaller for GaAs than 5 HR-silicon. The main contribution to the differential THz signal is thus from the spectral filter owing to the spatial confinement of the THz pulse in the pump area.

Example two, copper pathacyonine pellet. Pathacyonines are important dye molecules with excellent light harvesting capabilities, and their biomedical applications have been extensively investigated. The molecular structure of copper pathacyonine 10 (CuPc) is shown in Fig. 3. The optical absorption of CuPc peaks at 678 nm and overlaps with the spectrum of the pump laser pulse (centre wavelength 790 nm, bandwidth 100nm). Fig. 4 shows the THz transient transmitted through a CuPc pellet measured in the presence and absence of visible laser excitation. The main THz pulses measured with and without laser excitation are almost identical, suggesting that 15 most frequency components in the absorption spectrum do not change under laser excitation. However, the smaller amplitude ripples after the main pulse in the time domain are different, indicating that some absorption features are changed by the laser excitation. The Fourier transforms of the measured THz transients are calculated and the ratio of their amplitudes is plotted in Fig. 4, together with the relative phase 20 difference. We observe features at 1.08 THz and 1.26 THz. This result represents evidence of a light-induced vibrational mode change in the THz frequency range.

We do not believe that the observed change is results from the mobile electrons, which is the main cause for the differential THz signal in semiconductors. Instead, the observed peak is due to the change in the environment surrounding the 25 vibrational modes. The energy associated with vibration modes in the THz frequency range is about 4 meV, corresponding to a temperature difference (kT) of 47 °C. Therefore a few degrees change in temperature is sufficient to cause substantial change in either the intensity or the frequency of the THz vibrational modes.

The present invention has significant implications for THz medical imaging. The 30 resolution of a THz imaging system is ultimately limited by the wavelength of the THz wave and although near field optics can be used to obtain higher resolution images, this can not be applied to in vivo THz imaging beneath, for example, the surface of skin. As is provided by the present invention, the effective spot size of a THz pulse can be spatially confined to the pump area of a sample, which is determined by the

focussed size of the visible pump laser beam. Therefore the resolution of a differential THz imaging system is ultimately limited by the spot size of the visible pump beam rather than the THz wavelength.

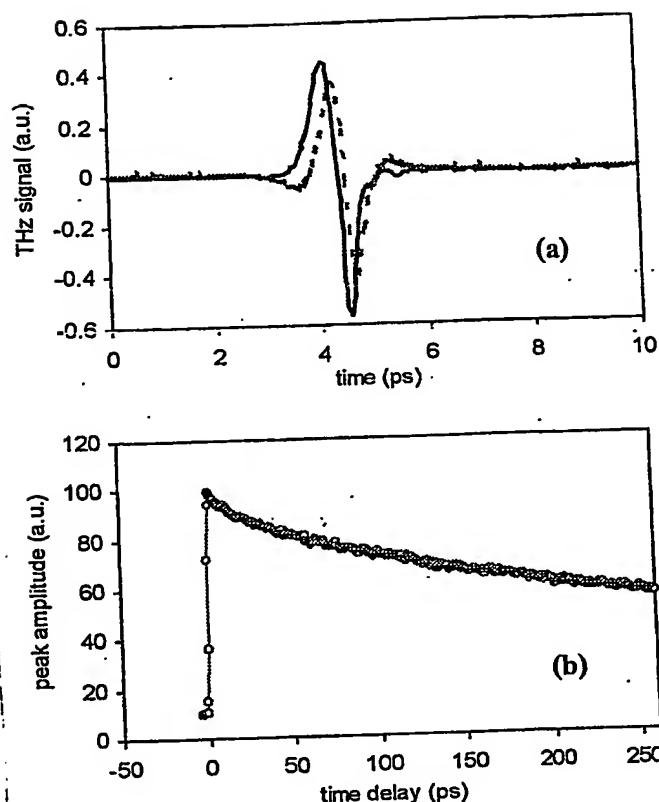


Fig 1.

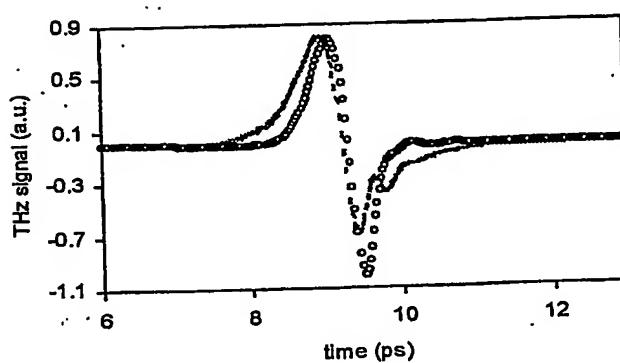


Fig 2.

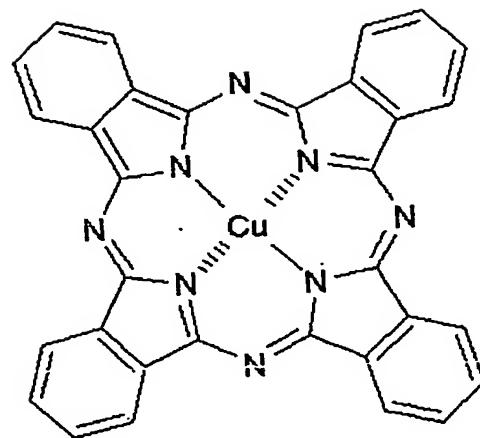


Fig. 3

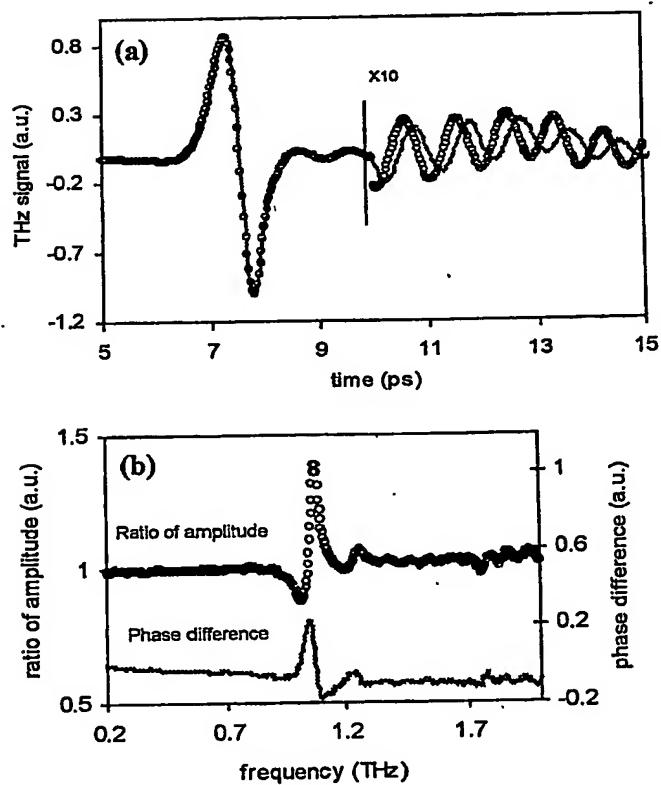
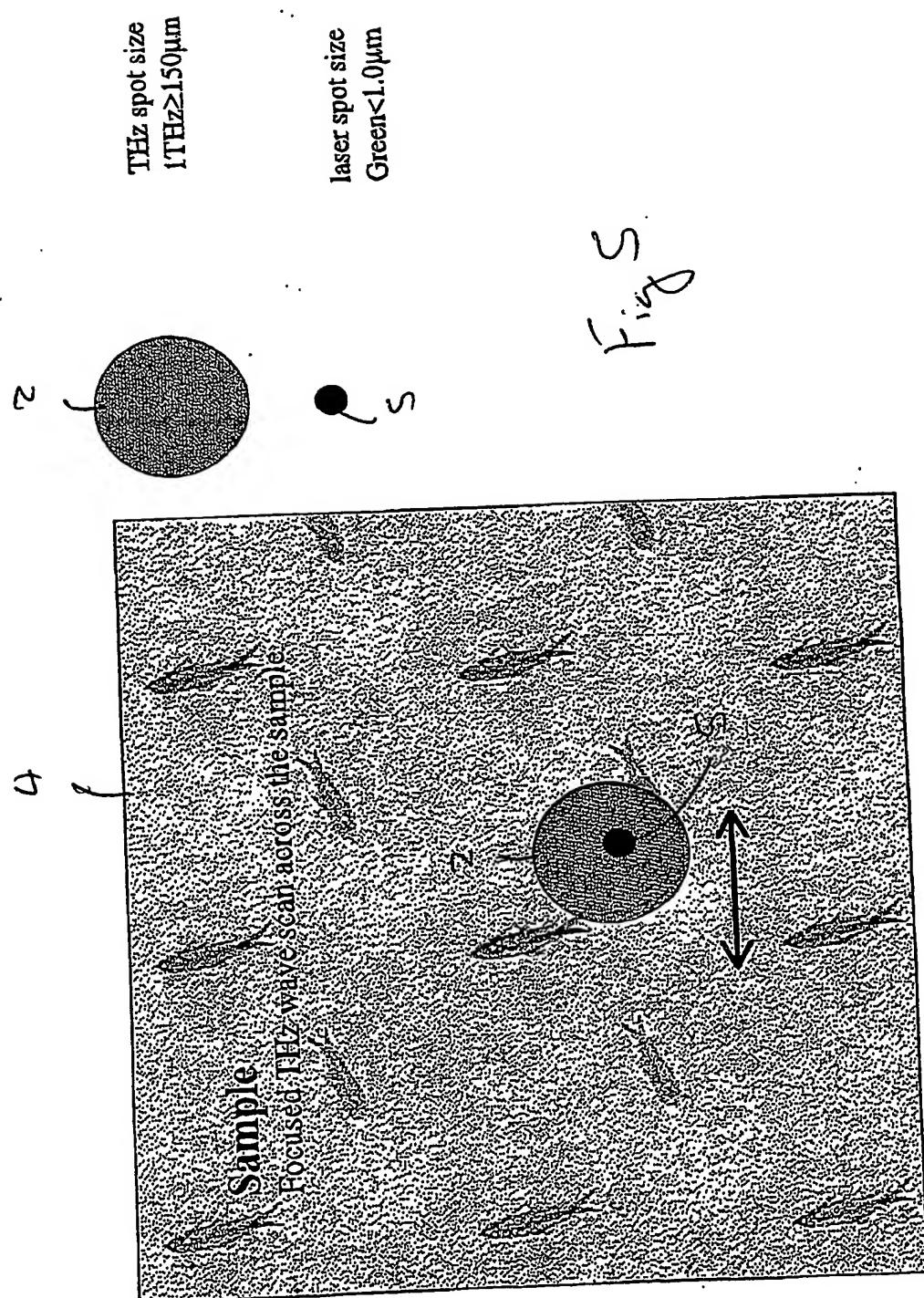
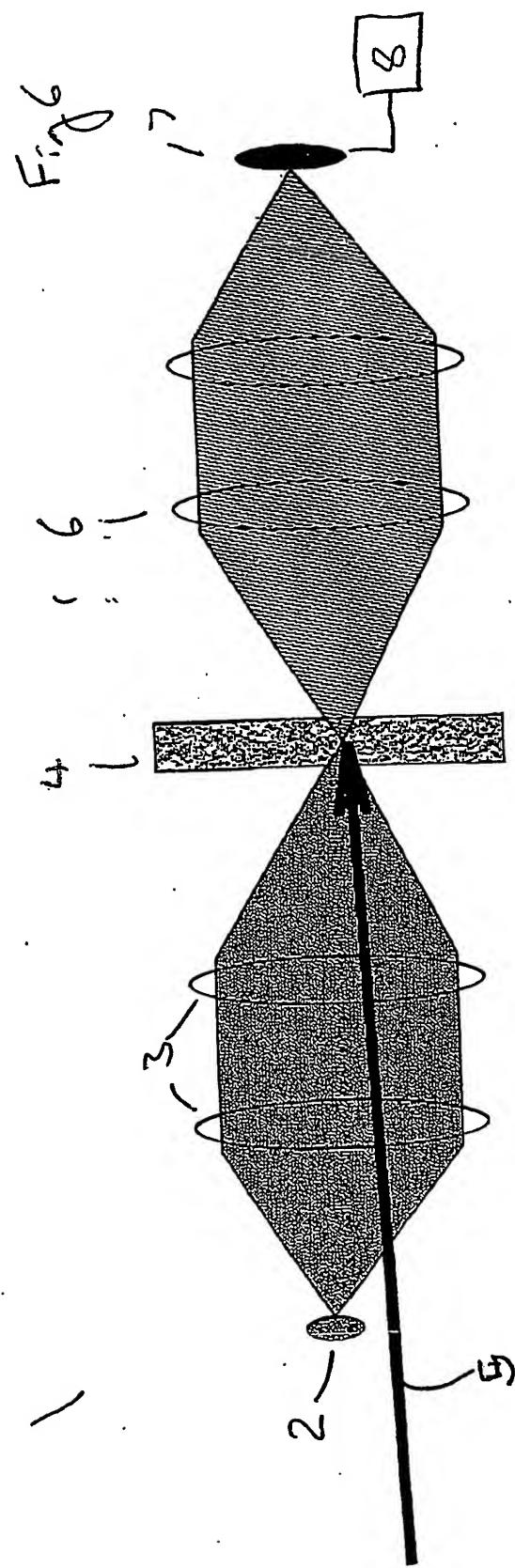


Fig. 4





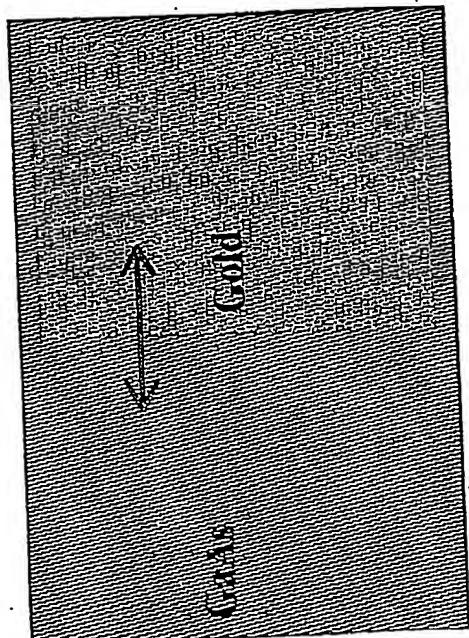
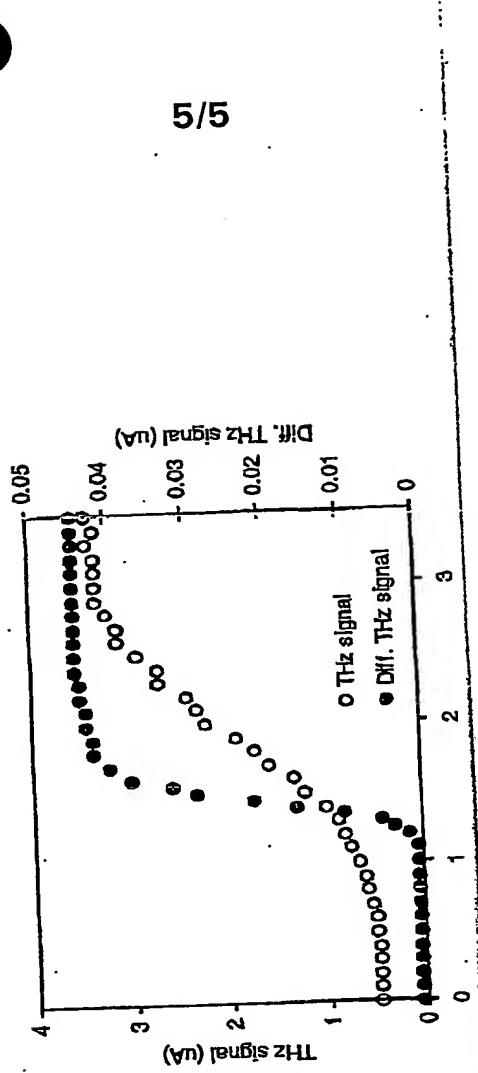


Fig. 7